

### **REMARKS**

Claims in the case are 1-19, upon entry of this amendment. Claims 1-17 have been amended, Claims 18 and 19 have been added, and no claims have been cancelled herein.

The claims have been amended herein for purposes of formality by, for example, rearranging terms, introducing indentation, replacing "characterized in that" with --wherein--, replacing "according to" with --of--, and including Markush language.


Basis for added Claim 18 is found in original Claim 1, and at page 5, lines 18-31 of the specification. Basis for added Claim 19 is found in original Claim 16, and at page 5, lines 18-31 of the specification.

The specification has been amended herein to include section headings. The title has been amended to correspond to that of the related International Patent Publication No. WO 2005/007327 A2. In addition, the specification has been amended to include a Brief Description of the Drawings. Basis for the brief descriptions of Figures 1-6 is found in Example 1 at page 22, line 6 through page 24, line 26 of the specification. Basis for the description of Figure 7 is found at lines 1-8 on page 16 of the specification.

Included herewith is a Substitute Specification (excluding claims) in accordance with 37 C.F.R. §§ 1.52, 1.121(b)(3) and 1.125(b), and an annotated copy of the specification (excluding claims) in accordance with 37 C.F.R. § 1.125(c). In accordance with 37 C.F.R. § 1.121(b), Applicants' undersigned attorney states that the Substitute Specification includes no new matter. In accordance with 37 C.F.R. § 121(b)(3)(i) Applicants respectfully instruct the Office to replace the specification with the Substitute Specification.

The amendments presented herein are not deemed to represent the entry of new matter into the application. Applicants respectfully request entry of this Preliminary Amendment.

Respectfully submitted,

By   
James R. Franks  
Attorney for Applicants  
Reg. No. 42,552

Bayer MaterialScience LLC  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741  
(412) 777-3808  
FACSIMILE PHONE NUMBER:  
(412) 777-3902

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~~Method for producing fine metal, alloy and composite powders~~

**METHOD FOR THE PRODUCTION OF FINE METAL POWDER, ALLOY  
POWDER AND COMPOSITE POWDER**

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**FIELD OF THE INVENTION**

The invention relates to a method for producing metal, alloy or composite powders with a mean particle diameter D50 of at most 25  $\mu\text{m}$ , a starting powder firstly being formed into flake-like particles and these then being comminuted in the presence of grinding aids, and to metal, alloy or composite powders obtainable thereby.

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**BACKGROUND OF THE INVENTION**

Numerous metallurgical or chemical methods are known for producing metal and alloy powders. If fine powders are to be produced, the known methods frequently start with the melting of a metal or an alloy.

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If the melt is divided by atomisation, the powder particles form directly from the produced melt droplets by solidification. A large number of possibilities, but also limitations to the process, arise depending on the type of cooling (treatment with air, inert gas, water), the process engineering parameters used, for instance the nozzle geometry, gas speed, gas temperature or the nozzle material, and the material parameters of the melt, such as melting and solidification points, solidification behaviour, viscosity, chemical composition and reactivity with the process media (W. Schatt, K.-P. Wieters in "Powder Metallurgy – Processing and Materials", EPMA European Powder Metallurgy Association, 1997, 10 to 23).

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As powder production by atomisation is of particular industrial and economic significance, various atomisation strategies have become established. Specific methods are selected depending on the powder properties required, such as particle size, particle size distribution, particle morphology, impurities, and properties of the melts to be atomised, such as melting point or reactivity, and the tolerable costs. Nevertheless there are often limits from economic and industrial points of view to attaining a specific property profile of the powder (particle size distributions,

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impurity contents, “designated size” yield, morphology sintering activity, etc.) at justifiable costs (W. Schatt, K.-P. Wieters in “Powder Metallurgy – Processing and Materials”, EPMA European Powder Metallurgy Association, 1997, 10 to 23).

- 5 Powder production by atomisation primarily has the drawback that large quantities of energy and atomising gas have to be used, and this renders the procedure very expensive. In particular production of fine powder from high melting alloys with a melting point  $> 1,400^{\circ}\text{C}$  is not very economical as, on the one hand, the high melting point necessitates a very high application of energy for producing the melt and, on
- 10 the other hand, the gas consumption greatly increases as the desired particle size decreases. In addition, difficulties often occur if at least one alloy element has a very high affinity to oxygen. Cost advantages may be achieved during production of particularly fine alloy powder by using specially developed nozzles.
- 15 In addition to particle production by atomisation, other single-stage melt metallurgical methods are also frequently used, such as what is known as “melt-spinning”, i.e. pouring a melt onto a cooled roll, whereby a thin, usually easily comminutable strip is produced, or what is referred to as “crucible melt extraction”, i.e. the immersion of a cooled profiled roll rotating at high speed into a molten
- 20 metal, wherein particles or fibres are obtained.

- A further important variant of powder production is the chemical method via reduction of metal oxides or metal salts. However, it is not possible to obtain alloy powders in this manner (W. Schatt, K.-P. Wieters in “Powder Metallurgy –
- 25 Processing and Materials”, EPMA European Powder Metallurgy Association, 1997, 23 to 30).

- Extremely fine particles which have particle sizes of less than one micrometre may also be produced by the combination of evaporation and condensation of metals and
- 30 alloys and via gas phase reactions (W. Schatt, K.-P. Wieters in “Powder Metallurgy – Processing and Materials”, EPMA European Powder Metallurgy Association, 1997, 39 to 41). These methods are very expensive, however.

If cooling of the melt takes place in a relatively large volume/block, mechanical method steps of coarse, fine and superfine comminution are necessary to produce metal or alloy powder that may be processed by powder metallurgy. An overview of mechanical powder production is given by W. Schatt, K.-P. Wieters in "Powder  
5 Metallurgy – Processing and Materials", EPMA European Powder Metallurgy Association, 1997, 5 to 47.

Mechanical comminution, in particular in mills, as the oldest method of particle size adjustment, is very advantageous from an industrial perspective as it inexpensive  
10 and may be applied to a large number of materials. However, it makes certain demands on the process material, for example with respect to size of the pieces and brittleness of the material. In addition, comminution cannot be pursued as desired; rather a grinding equilibrium forms, which also occurs if the grinding process is begun with relatively fine powders. The conventional grinding processes are  
15 modified if the physical limits of the capacity for comminution are attained for the respective grinding stock and certain phenomena, such as embrittlement at low temperatures or the effect of grinding aids, improve the grinding behaviour or the capacity for comminution.

20 A method of fine comminution of relatively brittle pre-comminuted material that is particularly suitable in many cases involves the concept of gas contra-jet mills of which there are numerous commercial suppliers, for example Hosokawa-Alpine or Netzsch-Condux. This method is prevalent and provides, in particular in the case of brittle materials, considerable advantages from industrial (low level of impurities,  
25 autogenic grinding) and financial perspectives compared to conventional mills using purely mechanical comminution, such as ball mills or agitated ball mills. Jet mills attain their industrial and thus their financial limits with comminution of ductile starting powders, in other words materials that are difficult to comminute, and low designated particle sizes. This is explained by the decreasing kinetic energy of the  
30 powder particles being comminuted in the gas jet. As the kinetic energy of the powder particles is to be applied only via the carrier gas, the specific energy requirement during superfine comminution increases to financially unjustifiable

ranges and in the case of powders with high ductility is practically inapplicable. The sintering activity of these powders thus comminuted does not correspond to the sintering activity of powder particles produced by conventional grinding either.

- 5 Very fine particles may be obtained, for example, by combining grinding steps with hydrogenation and dehydrogenation reactions, including the combination of reaction products to form the desired phase composition of the powder (I.R. Harris, C. Noble, T. Bailey, Journal of the Less Common Metals, 106 (1985), L1 to L4). However, this method is limited to alloys which contain elements that may form stable  
10 hydrides. Mechanical influences on the comminution in the form of lattice defects or other defects may thus be substantially avoided. This is particularly important if the functional properties of the powder particles, for example the crystallites, critically affect the properties of the powder product, such as in NdFeB permanent magnets.
- 15 Said methods always meet their limits if it is a matter of producing very fine powders of ductile metals or alloys which have both high reactivity to oxygen and high sintering activities.

The coldstream process was developed for producing products of this type, metallic  
20 particles subjected to intense cooling being centrifuged at extremely high speeds of up to 1 Mach via a venturi tube onto a cooled panel. It is thus allegedly possible to produce a product with a particle size between 5 and 10  $\mu\text{m}$  (W. Schatt, K.-P. Wieters in "Powder Metallurgy – Processing and Materials", EPMA European Powder Metallurgy Association, 1997, 9 to 10). The act of accelerating the starting  
25 powder to the speed of sound necessitates an extremely high application of energy in this method. Furthermore, abrasion problems may occur and, owing to the interaction between particles and counterplate, critical impurities are introduced into the grinding stock.

- 30 A further method for producing fine powder from ductile material is mechanical alloying. In this process agglomerates are obtained by intensive grinding treatment, which agglomerates are made up of crystallites that are approximately 10 to 0.01  $\mu\text{m}$

in size. The metallic ductile material changes as a result of the high mechanical stress in such a way that fine individual particles may possibly form. These contain the composition typical of the alloy. However, the drawback of this process is that considerable impurities are sometimes introduced, primarily by abrasion. Usually, however, it is precisely the uncontrolled abrasion that is an obstacle to industrial use. In addition there is the fact that discrete superfine particles are only produced after a very long grinding period. Fine metal and alloy powders therefore cannot be economically produced by mere mechanical alloying.

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### **SUMMARY OF THE INVENTION**

The object of the present invention therefore consists in providing a process for producing fine, in particular ductile, metal, alloy or composite powders, the method being particularly suitable for producing alloys, i.e. multi-component systems, and allowing fundamental properties, such as particle size, particle size distribution, sintering activity, impurity content or particle morphology to be purposefully adjusted or influenced.

The object is achieved according to the invention by a two-stage method, a starting powder firstly being formed into flake-like particles and these then being comminuted in the presence of grinding aids.

The invention therefore relates to a method for producing metal, alloy or composite powders with a mean particle diameter D50 of at most 25  $\mu\text{m}$ , determined using the particle measuring apparatus Microtrac® X 100 to ASTM C 1070-01, from a starting powder with a greater mean particle diameter, wherein

a) the particles of the starting powder are processed in a shaping step into flake-like particles, of which the particle diameter to particle thickness ratio is between 10:1 and 10,000:1, and

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b) the flake-like particles are subjected to comminution grinding in the presence of a grinding aid.

b) the flake-like particles are subjected to comminution grinding in the presence of a grinding aid.

The particle measuring apparatus Microtrac® X 100 is commercially available from Honeywell, U.S.A.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

- Figure 1 is a scanning electron microscope ("SEM") image (magnification = 300X) of a starting (or feed) nickel alloy powder;
- Figure 2 is an SEM image (magnification = 300X) of flakes resulting from a deformation process step performed on starting nickel alloy powder;
- Figure 3 is an SEM image (magnification = 1000X) of material obtained from comminution grinding of flakes obtained from a deformation process of starting nickel alloy powder;
- Figure 4 includes representative particle size distribution plots of deagglomerated primary nickel alloy particles that were deagglomerated by means of ultrasound treatment of agglomerated primary particles in isopropanol;
- Figure 5 includes representative particle size distribution plots of deagglomerated primary nickel alloy particles that were deagglomerated by subjecting agglomerated primary particles to gas contrajet mill treatment followed by ultrasound treatment in isopropanol;
- Figure 6 is an SEM image (magnification = 600X) of deagglomerated nickel alloy particles after being subjected to gas contrajet mill treatment; and
- Figure 7 is a representative plot of contraction (S) and contraction rate (AS) for a comparative powder (V) and a powder prepared according to the present invention (PZD) as a function of standardized temperature ( $T_N$ ).

For a further detailed discussion of Figures 1-6, see Example 1 herein.



### **DETAILED DESCRIPTION OF THE INVENTION**

For determining the particle diameter to particle thickness ratio the particle diameter and the particle thickness are determined using a light-optical microscope. For this purpose, the flake-like powder particles are firstly mixed with a viscous, transparent epoxy resin in a ratio of 2 volume fractions resin and 1 volume fraction flakes. The air bubbles introduced during mixing are then expelled by evacuation of this mixture. The then bubble-free mixture is poured over a planar substrate and then rolled out using a roller. The flake-like particles are thus oriented in the flow field between roller and substrate. The preferred position manifests itself in that the surface normals of the flakes are oriented on average parallel to the surface normals of the planar substrate, in other words the flakes are arranged in layers on average flat on the substrate. After curing, suitable samples of suitable dimensions are worked from the epoxy resin plate on the substrate. The samples are microscopically examined perpendicularly and parallel to the substrate. By using a microscope with a calibrated lens and by taking into account the adequate particle orientation at least 50 particles are measured and an average is formed from the measured values. This average represents the particle diameter of the flake-like particles. Following a perpendicular cut through the substrate and the sample to be examined, the particle thicknesses are determined using the microscope with a calibrated lens, which microscope was also used to determine the particle diameter. Care should be taken that only particles located optimally parallel to the substrate are measured. As the particles are completely surrounded by the transparent resin, selecting suitably oriented particles and reliably assigning the limitations of the particles to be evaluated do not present any difficulties. Again at least 50 particles are measured and an average formed from the measured values. This average represents the particle thickness of the flake-like particles. The particle diameter to particle thickness ratio is calculated from the previously ascertained values.

In particular fine, ductile metal, alloy or composite powders may be produced with the method according to the invention. Ductile metal, alloy or composite powders are in this case taken to mean those powders which, in the event of mechanical stress until the yield point is reached, undergo plastic expansion or deformation before

significant material damage (material embrittlement, material rupture) occurs. Plastic material changes of this type are dependent on the material and are in the range of 0.1 per cent up to several 100 per cent, based on the starting length.

- 5     The degree of ductility, i.e. the capacity of materials to plastically, i.e. permanently, deform under the effect of mechanical stress may be determined or described by mechanical tensile or pressure testing.

For determining the degree of ductility by tensile testing what is referred to as a  
10     tensile sample is produced from the material to be assessed. This may be, for example, a cylindrical sample which, halfway along its length, has a reduction in diameter of approximately 30 to 50 % over a length of approximately 30 to 50 % of the total sample length. The tensile sample is fixed in a fixing device of an electromechanical or electrohydraulic tensile testing machine. Length sensors are  
15     installed on average of the sample over a measuring length which is approximately 10 % of the overall sample length, before actual mechanical testing. These sensors allow the increase in the length to be followed in the selected measuring length during application of a mechanical tensile stress. The stress is increased until the sample fractures and the plastic content of the change in length is evaluated using  
20     the stress-strain recording. Materials which achieve a plastic change in length of at least 0.1 % in an arrangement of this type will be called ductile in the context of this specification.

Analogously it is also possible to subject a cylindrical material sample, which has a  
25     diameter to thickness ratio of approximately 3:1, to mechanical compressive stress in a commercially available pressure testing machine. Permanent deformation of the cylindrical sample occurs in this case as well after application of an adequate mechanical compressive stress. Once the pressure has been relieved and the sample removed, an increase in the diameter to thickness ratio of the sample is determined.  
30     Materials which achieve a plastic change of at least 0.1 % in a test of this type are also called ductile in the context of this specification.

Fine ductile alloy powders which have a degree of ductility of at least 5 % are preferably produced by the method according to the invention.

According to the invention the capacity for comminution of alloy or metal powders that cannot be comminuted further *per se* is improved by the use of mechanically, mechanochemically and/or chemically acting grinding aids which are purposefully added or produced in the grinding process. A fundamental aspect of this approach is that the chemical "desired composition" of the powder thus produced cannot be changed overall or influenced even such that the processing properties, such as the sintering behaviour or flowability, are improved.

The method according to the invention is suitable for producing a wide variety of fine metal, alloy or composite powders with a mean particle diameter D50 of at most 25 µm.

For example metal, alloy or composite powders of a composition corresponding to formula I

$$hA-iB-jC-kD \quad (I)$$

may be obtained, wherein

- A represents one or more of the elements Fe, Co, Ni,
- B represents one or more of the elements V, Nb, Ta, Cr, Mo, W, Mn, Re, Ti, Si, Ge, Be, Au, Ag, Ru, Rh, Pd, Os, Ir, Pt,
- C represents one or more of the elements Mg, Al, Sn, Cu, Zn, and
- D represents one or more of the elements Zr, Hf, rare-earth metal,

and h, i, j and k indicate the percentages by weight, wherein

h, i, j and k in each case independently of one another represent 0 to 100 % by weight,

with the proviso that the sum of h, i, j and k is 100 % by weight.

In formula I preferably

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- A represents one or more of the elements Fe, Co, Ni,
- B represents one or more of the elements V, Cr, Mo, W, Ti,
- C represents one or more of the elements Mg, Al and
- D represents one or more of the elements Zr, Hf, Y, La.

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h preferably represents 50 to 80 % by weight, in particular preferably 60 to 80 % by weight. i preferably represents 15 to 40 % by weight, in particular preferably 18 to 40 % by weight. j preferably represents 0 to 15 % by weight, in particular preferably 5 to 10 % by weight. k preferably represents 0 to 5 % by weight, in particular preferably 0 to 2 % by weight.

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The metal, alloy or composite powders produced according to the invention are distinguished by a small mean particle diameter D<sub>50</sub>. The mean particle diameter D<sub>50</sub> is preferably at most 15 µm, determined to ASTM C 1070-01 (measuring apparatus: Microtrac® X 100).

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By way of example powders which already have the composition of the desired metal, alloy or composite powder may be used as the starting powder. In the method according to the invention however, it is also possible to use a mixture of several starting powders which only produce the desired composition after suitable selection of the mixing ratio. The composition of the produced metal, alloy or composite powder may also be influenced by the choice of grinding aid, if this remains in the product.

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Powders with spherical or irregularly shaped particles and a mean particle diameter D<sub>50</sub>, determined to ASTM C 1070-01 of greater than 25 µm, preferably 30 to 2,000

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µm, in particular preferably 30 to 1,000 µm, are preferably used as the starting powders.

5 The required starting powders may be obtained, for example, by atomisation of molten metals and, if necessary, subsequent screening or sifting.

According to the invention the starting powder is firstly subjected to a deformation step. The deformation step may be carried out in known devices, for example in a rolling mill, an eddy mill, a high-energy mill or an attritor or an agitated ball mill.  
10 By suitably selecting the process engineering parameters, in particular as a result of the effect of mechanical stresses which are sufficient to achieve plastic deformation of the material or the powder particles, the individual particles are deformed, so they ultimately have a flake-like form, the thickness of the flakes preferably being 1 to 20 µm. This may take place, for example, by one-off stressing in a roller or a hammer mill, by repeated stressing in “small” deformation steps, for example by percussive grinding in an eddy mill or a Simoloyer®, or by a combination of percussive and  
15 frictional grinding, for example in an attritor or a ball mill. The high material stress during this deformation may lead to structural damage and/or material embrittlement which may be used in the following steps for comminuting the material.

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Known molten metallurgical fast solidification processes may also be used for producing strips or “flakes”. These, like the mechanically produced flakes, are then suitable for comminution grinding described below.

25 The device in which the deformation step is carried out, the grinding media and the other grinding conditions are preferably selected such that the impurities as a result of abrasion and/or reactions with oxygen or nitrogen are as small as possible and below the critical value for the application of the product or are within the specification relevant to the material.

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This is possible for example by suitable selection of the grinding container and grinding media materials and/or the use of gases hindering oxidation and nitriding and/or the addition of protecting solvents during the deformation step.

- 5 In a particular embodiment of the method according to the invention the flake-like particles are produced in a fast solidification step, for example by what is known as “melt spinning”, directly from the melt by cooling on or between one or more, preferably cooled roller(s), so flakes are directly formed.
- 10 According to the invention the flake-like particles obtained in the deformation step are subjected to comminution grinding. In the process, on the one hand, the particle diameter to particle thickness ratio changes, primary particles with a particle diameter to particle thickness ratio of 1:1 to 10:1 usually being obtained and, on the other hand, the desired mean particle diameter of at most 25  $\mu\text{m}$  is adjusted without
- 15 particle agglomerates that are difficult to comminute occurring again.

Comminution grinding may take place for example in a mill, for instance an eccentric mill, but also in Gutbett rolls, extruders or similar devices which bring about material shattering owing to different movement and stress rates in the flake.

- 20 According to the invention comminution grinding is carried in the presence of a grinding aid. Liquid grinding aids, waxes and/or brittle powder for example, may be used as the grinding aid. In this case the grinding aids may act mechanically, chemically or mechanochemically.

- 25 By way of example the grinding aid may be paraffin oil, paraffin wax, metal powder, alloy powder, metal sulphides, metal salts, salts of organic acids and/or hard material powder.

- 30 Brittle powder or phases act as mechanical grinding aids and may be used, for example, in the form of alloy, element, hard material, carbide, silicide, oxide, boride, nitride or salt powder. By way of example pre-comminuted element and/or alloy

powders are used which, together with the starting powder used, which is difficult to comminute, produce the desired composition of the product powder.

5 Brittle powders used are preferably those which comprise binary, ternary and/or higher compositions of the elements A, B, C and/or D that occur in the starting alloy used, A, B, C and D having the meanings given above.

10 Liquid and/or easily deformable grinding aids, for example waxes, may also be used. Other examples include hydrocarbons, such as hexane, alcohols, amines or aqueous media. These are preferably compounds which may be required for the following steps of further processing and/or which may be easily removed after comminution grinding.

15 It is also possible to use specific organic compounds which are known from pigment production where they are used to stabilise non-agglomerating individual flakes in a liquid environment.

20 In a particular embodiment grinding aids are used which enter a targeted chemical reaction with the starting powder to achieve the grinding progress and/or for adjusting a specific chemical composition. These may be, for example, decomposable chemical compounds, of which only one or more constituents are required for adjusting a desired composition, it being possible to substantially remove at least one component or constituent by a thermal process.

25 Reducible and/or decomposable compounds, such as hydrides, oxides, sulphides, salts and sugars are mentioned as examples which are at least partially removed from the grinding stock in a subsequent processing step and/or powder metallurgical processing of the product powder, the remaining residue chemically complementing the powder composition in the desired manner.

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It is also possible that the grinding aid is not added separately but is produced *in situ* during comminution grinding. In this case the procedure may, for example, be such

that the grinding aid is produced by adding a reactive gas which reacts under the conditions of comminution grinding with the starting powder while forming a brittle phase. Hydrogen is preferably used as the reactive gas.

- 5 The brittle phases which are produced during treatment with the reactive gas, for example by formation of hydrides and/or oxides, may usually be removed again by appropriate method steps after comminution grinding or during processing of the fine metal, alloy or composite powder obtained.
- 10 If grinding aids are used which are not removed, or are only partially removed, from the metal, alloy or composite powder produced according to the invention, they are preferably selected such that the remaining constituents affect a property of the material in a desired manner, such as improving the mechanical properties, reducing the corrodibility, increasing the hardness and improving the abrasion behaviour or
- 15 the frictional and sliding properties. The use of a hard material is mentioned here by way of example, which is increased in content in a subsequent step to the extent that the hard material may be further processed with the alloy component to form a hard metal or a hard material alloy composite.
- 20 After the deformation step and comminution grinding the primary particles of the metal, alloy or composite powder produced have, according to the invention, a mean particle diameter D50, determined to ASTM C 1070-01 (Microtrac® X 100), of at most 25 µm.
- 25 In addition to the formation of fine primary particles, the known interactions between superfine particles can lead to the formation of relatively coarse secondary particles (agglomerates), of which the particle diameter is far greater than the desired mean particle diameter of at most 25 µm, despite the use of grinding aids.
- 30 A deagglomeration step therefore preferably follows comminution grinding, during which the agglomerates are broken open and the primary particles liberated. Deagglomeration may, for example, take place by applying shear forces in the form



of mechanical and/or thermal stresses and/or by removing separation layers previously introduced in the process between primary particles. The deagglomeration methods to be applied in particular are oriented toward the degree of agglomeration, the intended use and the susceptibility to oxidation of the superfine powder and the admissible impurities in the finished product.

Deagglomeration may, for example, take place by mechanical methods, for instance by treatment in a gas contrajet mill, screening, sieving or treatment in an attritor, a kneader or a rotor-stator dispergator. The use of a stress field, as generated in ultrasound treatment, thermal treatment, for example dissolution or conversion of a previously introduced separating layer between the primary particles by cryo- or high-temperature treatments, or a chemical conversion of introduced or purposefully produced phases, is also possible.

Deagglomeration is preferably carried out in the presence of one or more liquids, dispersing aids and/or binders. A slurry, a paste, a kneading compound or a suspension with a solids content between 1 and 95 % by weight may thus be obtained. Solids contents between 30 and 95 % by weight may be directly processed by known powder technological processes such as injection moulding, film casting, coating, and hot-moulding, and are then reacted in suitable steps of drying, releasing and sintering to form an end product.

A gas contrajet mill, which is operated under inert gases, such as argon or nitrogen, is preferably used for deagglomeration of particularly oxygen-sensitive powders.

The metal, alloy or composite powders produced according to the invention are distinguished from conventional powders with identical mean particle diameters and identical chemical composition which are produced, for example, by atomisation, by a range of particular properties.

The invention therefore also relates to metal, alloy or composite powders with a mean particle diameter D50 of at most 25  $\mu\text{m}$ , determined using the particle

measuring apparatus Microtrac® X 100 to ASTM C 1070-01, which are obtainable by the method according to the invention.

5 The metal, alloy and composite powders according to the invention exhibit, for example, excellent sintering behaviour. At low sintering temperatures the same sintering densities may be attained as in powders produced by atomisation. Starting from powder compacts of a defined compressed density, higher sintering densities may be achieved at the same sintering temperature. This increased sintering activity is also exhibited, for example, in the fact that, until the maximum contraction is  
10 attained, the contraction during the sintering process is greater than in conventionally produced powders.

The invention therefore also relates to metal, alloy or composite powders with a mean particle diameter D50 of at most 25 µm, determined using the particle  
15 measuring device Microtrac® X 100 to ASTM C 1070-01, wherein, until the maximum contraction is attained, the contraction, determined using a dilatometer to DIN 51045-1 has at least 1.05 times the contraction of a metal, alloy or composite powder with identical chemical composition and identical mean particle diameter D50, the powder to be investigated being compressed to a compressed density of 50  
20 % of the theoretical density before the contraction is measured.

The powder to be investigated may be compressed by adding conventional compression-assisting agents, such as paraffin wax or other waxes or salt or organic acids, for example zinc stearate.

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Metal, alloy or composite powders which are produced by atomisation and by comparison with which the powders according to the invention have improved sintering behaviour, are to be taken to mean those powders which are produced by conventional atomisation known to the person skilled in the art.

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The advantageous sintering behaviour of the metal, alloy or composite powders according to the invention may also be recognised in the course of sintering and contraction curves, as shown, for example, in Fig. 7.

- 5 Fig. 7 shows, for a comparison powder (V) and a powder (PZD) according to the invention, the course of the contraction S or the contraction rate AS in each case in relative units as a function of the temperature  $T_N$  standardised to the respective sintering temperature  $T_S$ .
- 10 The comparison powder (V) is a product produced by atomisation under inert conditions and with a composition corresponding to that of the material described in Example 1 and the morphology of this powder. The particle size distribution (D50 approximately 8.4  $\mu\text{m}$ ) corresponds to that as shown in Fig. 5. The powder (PZD) according to the invention is a powder produced according to Example 1 with the
- 15 morphology illustrated in Fig. 6 and an oxygen content of 0.4 % by weight.

- After mixing with 3 % by weight microwax as the compression-facilitating additive powder compacts were produced from the two powders in a compression mould by applying a single-axle pressure of 400 to 600 mPa. The green density was in both
- 20 cases approx. 40 % of the theoretical density. These compacts were accordingly sintered individually in a dilatometer to DIN 51045-1 under protective gas conditions and using argon as the process gas. Heating at a rate of approx. 1 K/min (corresponding to approx.  $6 \cdot 10^{-4} \cdot T_S/\text{min}$ , where  $T_S$ : approx. 1,600 K) took place in the process. The push rod of the dilatometer does not exert any pressure on the
- 25 sample which supplies a measurable quantity for sintering contraction in the temperature range that is of interest for sintering (approx. 0.5  $T_S$  to approx. 0.95  $T_S$ ).

- The organic pressing aid is expelled to a temperature of approximately  $0.45 \cdot T_S$ . The actual sintering process takes place thereafter by further heating at the same
- 30 heating rate from approx. 0.5  $T_S$  to approx. 0.99  $T_S$ .

The advantages of the PZD powder lead to the following observations and to general rules which are illustrated with the aid of Fig. 7. For this purpose, the required terms, which allow a general description of the sintering processes, shall firstly be introduced:

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$^V T_{90}$  and  $^{PZD} T_{90}$ : temperatures (in standardised units according to  $T_N = T/T_S$ ) at which the two sintering bodies, at a heating rate of approx  $6 \cdot 10^{-4} \cdot T_S$ , have attained a contraction of 90 %, based on the same final contraction (= 100) attained.

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$^V T_{10}$  and  $^{PZD} T_{10}$ : temperatures (in standardised units according to  $T_N = T/T_S$ ) at which the two sintering bodies, at a heating rate of approx  $6 \cdot 10^{-4} \cdot T_S$ , have attained a contraction of 10 %, based on the same final contraction (= 100) attained.

15

$^V T_1$  and  $^{PZD} T_1$ : temperatures (in standardised units according to  $T_N = T/T_S$ ) at which the two sintering bodies, at a heating rate of approx  $6 \cdot 10^{-4} \cdot T_S$ , have attained a contraction of 1 %, based on the same final contraction (= 100) attained. Contraction starts at these temperatures.

20

$^V T_{max}$  and  $^{PZD} T_{max}$ : temperatures (in standardised units  $T_N = T/T_S$ ) at which the maximum contraction rate is reached.

$^V S(T_N)$ ,  $^{PZD} S(T_N)$ : contraction as a function of the standardised temperature  $T_N$ .

25

$^V AS(T_N)$ ,  $^{PZD} AS(T_N)$ : temperature-dependent contraction rate  $d(S(T_N))/dT_N$ , determined from the contraction curves to be compared  $^V S(T_N)$  and  $^{PZD} S(T_N)$ .

$^V S_{max}$  and  $^{PZD} S_{max}$ : maximum value of contraction rates, determined from the contraction curves derived according to temperature  $^V S(T_N)$  and  $^{PZD} S(T_N)$ .

30

The following general product properties of the powders according to the invention are obtained compared to conventionally produced atomised powders:

$$\frac{(PZD_{T_{\max}} - PZD_{T_{10}})}{PZD_{T_{\max}}} > \frac{(V_{T_{\max}} - V_{T_{10}})}{V_{T_{\max}}} \quad (I)$$

$$PZD_{T_{\max}} < V_{T_{\max}} \quad (II)$$

$$PZD_{T_{10}} < V_{T_{10}} \quad (III)$$

$$PZD_{T_1} < V_{T_1} \quad (IV)$$

$$5 \quad PZD_{S_{\max}} < V_{S_{\max}} \quad (V)$$

$$(PZD_{T_{\max}} - PZD_{T_{10}}) > (V_{T_{\max}} - V_{T_{10}}) \quad (VI)$$

$$(PZD_{T_{\max}} - PZD_{T_1}) > (V_{T_{\max}} - V_{T_1}) \quad (VII)$$

$$(PZD_{T_{90}} - PZD_{T_{10}}) > (V_{T_{90}} - V_{T_{10}}) \quad (VIII)$$

$$(PZD_{T_{90}} - PZD_{T_1}) > (V_{T_{90}} - V_{T_1}) \quad (IX)$$

10

The following conclusions with respect to the different behaviour of powder (PZD powder) produced according to the invention and comparison powders produced by conventional atomisation may be drawn from these inequalities:

- 15 - The sintering range for PZD powder is wider.
- The temperature at which contraction begins, at which, based on identical final contraction, 10 % of this final contraction is attained and at which contraction attains its maximum, is lower in PZD powders.
- 20 - The peaks of the contraction rates obtained from the standardised illustration of Fig. 7 mean that PZD powders have a lower contraction rate at  $PZD_{T_{\max}}$  than the comparison powder at  $V_{T_{\max}}$ .
- The initial temperature range up to the contraction peak is wider for PZD powders.
- 25 - The temperature range from the start of contraction up to the maximum contraction is greater for PZD powders.
- The temperature range between the temperature at which contraction of 10 % was attained up to the temperature at which contraction of 90 % was attained is greater for PZD powders.
- 30 - The temperature range from the start of contraction up to the temperature at which 90 % of the final contraction is attained is greater for PZD powders.

These statements relate to single-phase starting states of the powders. In the event that there are further phases not all of the inequalities (I) to (IX) have to always be met together, in particular very high contraction rates may occur locally on PZD powder compacts as a result of particular sintering activations of liquid phases, which rates constitute a further advantage with respect to processing capacity. However, the validity of the inequalities (III), (IV), (VIII) and (IX) is unaffected in this case as well.

The metal, alloy and composite powders according to the invention are distinguished, owing to a particular particle morphology with rough particle surface, moreover by outstanding compression behaviour and, owing to a comparatively broad particle size distribution, by high compressed density. This manifests itself in that compacts made of atomised powder have a lower bending strength, under otherwise identical production conditions, than the compacts made of powders according to the invention and with the same chemical composition and mean particle size D50. A further improvement in the compression behaviour may be achieved if powder mixtures comprising 1 to 95 % by weight metal, alloy or composite powders according to the invention and 99 to 5 % by weight atomised powder are used.

20

The sintering behaviour of powders produced according to the invention may also be purposefully influenced by the choice of grinding aid. Thus one or more alloys which, owing to their low melting point compared to the starting alloy form liquid phases during heating which improve the particle rearrangement and the material diffusion and thus the sintering behaviour and the contraction behaviour and thus allow higher sintering densities to be attained at the same sintering temperature or at lower sintering temperatures the same sintering density as may be achieved with the comparison powders, may be used as the grinding aid. Chemically decomposable compounds, of which the decomposition products with the basic material produce liquid phases or phases with increased diffusion coefficients which facilitate compression, may also be used.

30

X-ray analyses of the metal, alloy or composite powders according to the invention show a propagation of X-ray reflexes compared with X-ray reflexes that are obtained for powders with the same mean particle diameter and the same chemical composition which were obtained by atomisation. The propagation is demonstrated  
5 by the propagation of half widths. Usually the half widths of the X-ray reflexes are propagated by a factor  $> 1.05$ . This is caused by the mechanical stressed state of the particles, the existence of a higher dislocation density, i.e. disturbances to the solid in the atomic range, and the crystallite size in the particles. In the case of composite powders, alloy- and/or process-induced phases occur in the  
10 diffractograms in addition to the propagations of the X-ray reflexes of the main phase, which phases are significant for the contraction properties.

The method according to the invention allows production of metal, alloy and composite powders, in which oxygen, nitrogen, carbon, boron and silicon contents  
15 are purposefully adjusted. Oxide and/or nitride phases may form in the case of introduction of oxygen or nitrogen as a result of the high application of energy. Phases of this type may be desirable for specific applications as they may lead to strengthening of material. This effect is known as the "particle dispersion strengthening" effect (PDS effect). However, the introduction of such phases is  
20 often associated with a deterioration in the processing properties (for example compressibility, sintering activity). Owing to the generally inert properties of the dispersoids with respect to the alloy components, the latter may therefore have a sintering-inhibiting effect.

25 As a result of the comminution grinding to be carried out according to the invention, said phases are immediately superfinely distributed in the produced powder. The phases formed (for example oxides, nitrides, carbides, borides) are therefore much more finely and homogeneously distributed in the metal, alloy and composite powders according to the invention than in conventionally produced powders. This  
30 again leads to increased sintering activity compared with discretely introduced phases of the same kind.

The processing properties of the metal, alloy and composite powders according to the invention, for example the compression and sintering behaviour, and the capacity for processing by metal powder injection moulding (MIM), slurry-based methods or tape casting, may often be improved even further by adding metal, alloy  
5 or composite powders conventionally produced, in particular by atomisation.

The invention therefore also relates to mixtures containing 1 to 95 % by weight of a metal, alloy or composite powder and 99 to 5 % by weight of a conventionally  
10 produced metal, alloy or composite powder.

The mixtures according to the invention preferably contain 10 to 70 % by weight of a metal, alloy or composite powder according to the invention and 90 to 30 % by weight of a conventionally produced metal, alloy or composite powder.

15 The conventionally produced metal, alloy or composite powder according to the invention is preferably a powder which has been produced by atomisation.

The conventionally produced metal, alloy or composite powder may have the same chemical composition as the PZD powder contained in the mixture. Mixtures of this  
20 type are distinguished from pure PZD powders in particular by a further improvement in compression behaviour.

However, it is also possible that PZD powder and conventionally produced powder have a different chemical composition in the mixture. In this case the composition  
25 may be purposefully changed and as a result specific powder properties and consequently the material properties may be purposefully adjusted.

The following examples serve to describe the invention in more detail, wherein the examples are intended to facilitate understanding of the principle according to the  
30 invention and are not to be understood as a limitation thereof.



## Examples

The mean particle diameters D50 given in the examples were determined using a Microtrac® X 100 from Honeywell, U.S.A. to ASTM C 1070-01.

5

### Example 1

A Nimonic® 90 type alloy melt atomised by means of argon and with the composition Ni<sub>20</sub>Cr<sub>16</sub>Co<sub>2.5</sub>Ti<sub>1.5</sub>Al was used as the starting powder. The alloy powder obtained was screened between 53 and 25 µm. The density was approx. 8.2 g/cm<sup>3</sup>. The starting powder had substantially spherical particles, as may clearly be seen in Fig. 1 (scanning electron microscope image (SEM image) magnified 300 times).

15 The starting powder was subjected to deformation grinding in a vertical agitated ball mill (Netzsch Feinmahltechnik; PR 1S type), so the originally spherical particles assumed flake-like forms. The following parameters were used in particular:

- Grinding container volume: 5 l
- 20 • Speed of rotation: 400 rpm
- Circumferential speed: 2.5 m/s
- Ball filling: 80 vol.% (bulk volume of the balls)
- Grinding container material: 100Cr6 (DIN 1.3505: approx. 1.5 % by weight Cr, approx. 1 % by weight C, approx. 0.3 % by weight Si, approx. 0.4
- 25 % by weight Mn, < 0.3 % by weight Ni, < 0.3 % by weight Cu, remainder Fe)
- Ball material: hard metal (WC-10Co)
- Ball diameter: approx. 6 mm (total mass: 25 kg)
- Originally weighed in quantity of powder: 500 g
- Duration of treatment: 2 h
- 30 • Solvent: ethanol (approx. 2 l).

Fig. 2 is a SEM image magnified 300 times of the flakes produced in the deformation step. The high degree of material deformation, which was caused by the specific grinding treatment, compared with the starting powder may be seen. Damage to the structure of the material (crack formation) may also clearly be seen.

5

Comminution grinding was then carried out. That is referred to as an eccentric vibration grinding mill (Siebtechnik GmbH, ESM 324) with the following process engineering parameters was used:

- |    |  |
|----|--|
| 10 | <ul style="list-style-type: none"> <li>• Grinding container volume: 5 l operated as a satellite (diameter 20 cm, length approx. 15 cm)</li> <li>• Ball filling: 80 vol.% (bulk volume of the balls)</li> <li>• Grinding container material: 100 Cr6 (DIN 1.3505: approx. 1.5 % by weight Cr, approx. 1 % by weight C, approx. 0.3 % by weight Si, approx. 0.4</li> </ul> |
| 15 | <ul style="list-style-type: none"> <li>% by weight Mn, &lt; 0.3 % by weight Ni, &lt; 0.3 % by weight Cu, remainder Fe)</li> <li>• Ball material: 100 Cr6</li> <li>• Ball diameter: 10 mm</li> <li>• Originally weighed in quantity of powder: 150 g</li> </ul>   |
| 20 | <ul style="list-style-type: none"> <li>• Grinding aid 2 g paraffin</li> <li>• Oscillation amplitude: 12 mm</li> <li>• Grinding atmosphere: argon (99.998 %).</li> </ul>  |

After a grinding duration of 2 hours superfine particle agglomerates were obtained.

25

Fig. 3 is a SEM image magnified 1,000 times of the product obtained. The cauliflower-like structure of the agglomerate (secondary particle) may be seen, the primary particles having particle diameters of much less than 25 µm.

- 30 A sample of the primary particles or superfine particle agglomerates was subjected in a third method step to deagglomeration by ultrasound treatment in isopropanol in

an ultrasonic device TG 400 (Sonic Ultraschallanlagenbau GmbH) lasting 10 minutes at 50 % maximum power to obtain separated primary particles.

- The particle size distribution of the deagglomerated sample was determined using a
- 5 Microtrac® X 100 (manufacturer: Honeywell, U.S.A.) to ASTM C 1070-01. Fig. 4 shows the particle size distribution thus obtained. The D50 value of the starting powder was 40  $\mu\text{m}$  and was reduced to approx 15  $\mu\text{m}$  by the treatment according to the invention.
- 10 The remaining quantity of primary particles from comminution grinding were subjected in an alternative third method step to deagglomeration by treatment in a gas contrajet mill and subsequent ultrasound treatment in isopropanol in an ultrasonic device TG 400 (Sonic Ultraschallanlagenbau GmbH) at 50 % of the maximum power. The particle size was again determined using a Microtrac® X 100.
- 15 Fig. 5 shows the particle size distribution obtained. The D50 value was then only 8.4  $\mu\text{m}$ . This proves the possibility of further increasing the fine fraction in the powder produced according to the invention by high-energy post-treatment.

- Fig. 6 shows a SEM image (x 600 magnification) of the powder after treatment in
- 20 the gas contrajet mill. By using suitable screening methods it is accordingly possible to obtain alloy powders with even narrower particle size distribution. D50 values of less than approx. 8  $\mu\text{m}$  may thus be industrially and economically achieved.

- The introduced grinding aid paraffin may be removed during powder metallurgical
- 25 further processing of the alloy powder by thermal decomposition and/or evaporation and may be used as a compression aid.

- Example 2:** Production of Fe<sub>24</sub>Cr<sub>10</sub>Al<sub>11</sub>Y superfine powders using mechanical grinding aids without changing the composition of the starting
- 30 powder

500 g of a spherical starting powder of a Fe<sub>24</sub>Cr<sub>10</sub>Al<sub>1</sub>Y alloy with a mean particle diameter D<sub>50</sub> of 40 µm was processed to form flakes in a deformation stage under conditions analogous to those described in Example 1.

- 5 Comminution grinding was then carried out in an eccentric vibration grinding mill, as described in Example 1. A mixture of comminuted brittle Fe<sub>70</sub>Cr, Fe<sub>60</sub>Al and Fe<sub>16</sub>Y powders with a mean particle diameter of approx. 40 µm and fine Fe powder with a mean particle diameter D<sub>50</sub> of 10 µm was added as the grinding aid.
- 10 15 g grinding aid was used for comminution grinding. The addition of approx. 10 vol. % of a mechanically acting grinding aid is a typical content for this step. Smaller quantities of grinding aids may also be useful as a function of the proposed aim. The composition of the grinding aid used is summarised in Table 1. A mixture containing 65 % by weight Fe, 24 % by weight Cr, 10 % by weight Al and 1 % by
- 15 weight Y was obtained. The chemical composition of the starting powder is accordingly not altered by the choice of given alloy contents. A specific distribution of the components used (starting powder, grinding aid) is present in the composite powder obtained as a result of production according to the invention, so the composite powder undergoes a metallurgical change during further processing, for
- 20 example by sintering or another thermal process.

**Table 1** Composition of a mechanical grinding aid

Component	Quantity [g]	Fe [g]	Cr [g]	Al [g]	Y [g]
Fe <sub>16</sub> Y	0.93	0.78	0	0	0.15
Fe <sub>60</sub> Al	2.50	1.0	0	1.5	0
Fe <sub>70</sub> Cr	5.14	1.54	3.6	0	0
Fe	6.43	6.43	0	0	0
Total	15	9.75	3.6	1.5	0.15

- 25 A composite powder with a mean particle diameter D<sub>50</sub> of 15 µm was obtained after comminution grinding and deagglomeration in an ultrasonic field. It was possible to

obtain an alloy in the metallurgical sense from a composite powder of this type by thermal post-treatment.

**Example 3** Production of Fe<sub>24</sub>Cr<sub>10</sub>Al<sub>11</sub>Y superfine powders using mechanical grinding aids and changing the composition compared with the starting powder

In contrast to Example 2, a change in the chemical composition was desired or allowed during the grinding operation. An atomised alloy of composition Fe<sub>25,6</sub>Cr<sub>10,67</sub>Al with a mean particle diameter D<sub>50</sub> of 40 µm was subjected to a deformation step under the conditions described in Example 1. Flake-like particles with a mean particle diameter D<sub>50</sub> of 70 µm were obtained, of which the appearance did not significantly differ from that in Example 1.

Comminution grinding was then carried out. The procedure corresponded to that in Example 1 but 10 g of a Fe<sub>16</sub>Y powder with a mean particle diameter D<sub>50</sub> of 40 µm were used as the grinding aid and the grinding lasted 2 hours.

Table 2 gives the composition and quantity of flake-like starting alloy and the grinding aid added for comminution grinding.

**Table 2** Composition of the flake-like starting alloy and mechanical grinding aid used

Component	Quantity [g]	Fe [g]	Cr [g]	Al [g]	Y [g]
Fe <sub>25,6</sub> Cr <sub>10,67</sub> Al	150	95.6	38.4	16.0	0
Fe <sub>16</sub> Y	10	8.4	0	0	1.6
Total	160	104	38.4	16.0	1.6

As may be seen from Table 2, the composite powder obtained had the composition Fe<sub>24</sub>Cr<sub>10</sub>Al<sub>11</sub>Y. The composite powder was subjected to an ultrasound treatment after which a composite powder with a mean particle diameter D<sub>50</sub> of 13

µm was obtained.

#### Example 4

- 5 The procedure was as in Example 3, a mixture of a plurality of brittle materials and pure iron powder being used as the grinding aid.

Table 3 contains the composition and original weighed in quantities of the starting powder and grinding aid. The brittle grinding aids Fe60Al, Fe70Cr and Y2, 2H were  
10 brought to a mean particle diameter D50 of 40 µm before use in a separate grinding step. The Fe powder used had a mean particle diameter D50 of 10 µm.

**Table 3** Composition of the flake-like starting alloy and the mechanical grinding aid used

15

Component	Quantity [g]	Fe [g]	Cr [g]	Al [g]	Y [g]
Fe25,6Cr10, 67Al	150.00	95.60	38.40	16.00	0.00
Fe60Al	1.19	0.48	0.00	0.71	0.00
Fe70Cr	2.35	0.71	1.64	0.00	0.00
Y2,2H	1.66	0.00	0.00	0.00	1.66
Fe	10.00	10.00	0.00	0.00	0.00
Total	165.20	106.79	40.04	16.71	1.66

As may be seen from Table 3, the composite powder obtained had the composition Fe24Cr10Al11Y. The composite powder was subjected to an ultrasound treatment after which a composite powder with a mean particle diameter D50 of 15 µm was  
20 obtained.

**Example 5** Production of a Fe24Cr10Al11Y superfine powder from two FeCrAl master alloys and Fe16Y as the single brittle mechanical grinding aid

Flakes with mean particle diameters D50 of 70  $\mu\text{m}$ , of which the appearance did not significantly differ from the powder produced in Fig. 2, were produced in separate deformation steps analogously to Example 1 from two atomised alloys with the composition Fe19,9Cr24,8Al and Fe27,9Cr5Al with mean particle diameters D50 of 40  $\mu\text{m}$ .

The particularly brittle Fe16Y alloy was used as the only grinding aid during subsequent comminution grinding, which alloy had previously been comminuted to a mean particle diameter D50 of approx. 40  $\mu\text{m}$ . The procedure was as in Example 1, grinding lasting 2.5 hours.

Table 4 contains the composition and original weighed in quantities of the two flake-like FeCrAl starting alloys and of the brittle grinding aid (Fe16Y).

15

**Table 4** Composition of the flake-like starting alloys and the mechanical grinding aid used

Component	Quantity [g]	Fe [g]	Cr [g]	Al [g]	Y [g]
Fe19,9Cr24,8Al	43	23.8	8.6	10.5	0
Fe27,9Cr5Al	107	71.8	29.8	5.5	0
Fe16Y	10	8.4	0	0	1.6
Total	160	104	38.4	16	1.6

As may be seen from Table 3, the composite powder obtained had the composition Fe24Cr10Al1Y. The composite powder was subjected to an ultrasound treatment after which a composite powder with a mean particle diameter D50 of 12  $\mu\text{m}$  was obtained.

**Example 6** *In situ* production of the grinding aid

An atomised Ni<sub>15</sub>Co<sub>10</sub>Cr<sub>5,5</sub>Al<sub>4,8</sub>Ti<sub>3</sub>Mo<sub>1</sub>V alloy, which is commercially available under the model name IN 100®, was subjected, as described in Example 1, to a deformation step under an inert atmosphere.

5

No brittle grinding aid was added during subsequent comminution grinding, rather it was formed *in situ* during the grinding process. For this purpose, the eccentric vibration grinding mill was flooded with a gas mixture consisting of 94 vol. % argon and 6 vol. % hydrogen. The grinding container was thermally insulated, so a processing temperature of approx. 300 °C was established during the grinding process owing to the application of energy. The remaining grinding conditions corresponded to the procedure described in Example 1. The elevated temperature and the hydrogen content of the process gas lead to the formation of brittle Ti-H and V-H compounds which acted in the same manner as the grinding aids introduced in Examples 1 to 5 and thus led to comminution. After grinding that lasted 3 h under a hydrogen-containing atmosphere, an alloy powder with a mean particle diameter D<sub>50</sub> of 13 µm was achieved.

The chemical composition of the resultant superfine powder differed only slightly from that of the starting powder. The hydrogen content rose to < 1,000 ppm. During further processing of the alloy powder produced according to the invention the hydrogen content fell to below approx. 50 ppm again as a result of sintering under vacuum.

#### 25 **Example 7** Si powder as the mechanical grinding aid

Spherical atomised Ni<sub>38</sub>Cr<sub>8,7</sub>Al<sub>1,09</sub>Hf with a mean particle diameter D<sub>50</sub> of 40 µm was subjected, as described in Example 1, to a deformation step.

30 150 g of the flake-like powder produced in the attritor were subjected, as described in Example 1, to comminution grinding in an eccentric vibration grinding mill, 13 g Si powder with a mean particle diameter D<sub>50</sub> of 40 µm being added as the grinding



aid. After grinding that lasted 2 h an alloy powder with a mean particle diameter D50 of 10.5  $\mu\text{m}$  and the desired composition Ni<sub>35</sub>Cr<sub>8</sub>Al<sub>8</sub>Si<sub>1</sub>Hf was obtained. The silicon used is desirable or necessary in terms of alloy engineering. Of the possible brittle grinding aids Si is particularly suitable owing to its properties. After treatment  
5 the oxygen content was approx. 0.4 % by weight.

### Example 8

Spherical atomised Ni<sub>38</sub>Cr<sub>8,7</sub>Al<sub>1,09</sub>Hf with a mean particle diameter D50 of 40  $\mu\text{m}$   
10 was subjected, as described in Example 7 by using an attritor (agitated ball mill), to a deformation step.

Subsequent comminution grinding was carried out in the presence of Si powder (13 g) as the grinding aid, likewise in an agitated ball mill, the following technical  
15 parameters being adjusted:

- Grinding container volume: 5 l
- Ball filling: 80 vol. %
- Grinding container material: 100 Cr6
- 20 • Ball material: 100 Cr6
- Ball diameter: 3.5 mm
- Originally weighed in quantity of powder: 150 g Ni<sub>38</sub>Cr<sub>8,7</sub>Al<sub>1,09</sub>Hf
- Circumferential speed: 4.2 m/s
- Grinding liquid: ethanol
- 25 • Grinding duration: 1.5 h
- Grinding aid 13 g Si powder (D50: approx. 40  $\mu\text{m}$ )

After grinding that lasted 1.5 hours and subsequent ultrasonic deagglomeration an alloy powder with a mean particle diameter D50 of 13  $\mu\text{m}$ , measured by Microtrac®  
30 X 100, was obtained. The silicon used in this case was desirable or necessary in terms of alloy engineering in order to adjust the end composition

Ni38Cr8,7Al1,09Hf and in terms of process engineering for attaining the desired grinding effect. Of the elements that may be considered silicon is best suited as the grinding aid owing to its brittleness. This grinding process led to an increase in the oxygen content in the powder. At the conclusion of the grinding process the oxygen  
5 content was 0.4 % by weight.

### Example 9

A spherical atomised Ni17Mo15Cr6Fe5W1Co alloy with a mean particle diameter  
10 D50 of 40  $\mu\text{m}$ , which is commercially available under the name Hastelloy®, was subjected, as described in Example 1, to a deformation step.

The flake-like particles obtained were comminution ground in an eccentric vibration grinding mill in the presence of tungsten carbide as the grinding aid and under the  
15 following conditions:

- Grinding container volume: 5 l
- Ball filling: 80 vol. %
- Grinding container material: 100 Cr6
- 20 • Ball material: WC-10Co hard metal material
- Ball diameter: 6.3 mm
- Originally weighed in quantity of powder: 150 g
- Oscillation amplitude: 12 mm
- Grinding atmosphere: argon (99.998 %)
- 25 • Grinding duration: 90 minutes
- Grinding aid 13.5 g WC powder (D50 = 1.8  $\mu\text{m}$ )

The result of comminution grinding was an alloy hard material composite powder in which the alloy components had been comminuted to a mean particle diameter D50  
30 of approx. 5  $\mu\text{m}$  and the hard material component to a mean particle diameter D50

of approx. 1  $\mu\text{m}$ . The hard material particles were substantially homogenously distributed in the alloy powder volume.

The alloy hard material composite powder could be processed by conventional process steps to form a spray powder, For this purpose, 797 g WC with a mean particle diameter D50 to ASTM B 330 (FSSS) of 1  $\mu\text{m}$ , ethanol, PVA (polyvinyl alcohol) and suspension stabilisers were added to 163 g of the alloy hard material composite powder produced according to the invention for dispersing and generating a suspension. A suspension was produced which consisted to 25 vol. % of the metallic binding phase and to 75 vol. % of the WC hard material phase. This suspension was further processed by spray granulation and classification to form a green spray powder with a particle size of 20 to 63  $\mu\text{m}$ . The organic auxiliaries were firstly removed from this green spray powder by gas evolution at 100 to 400  $^{\circ}\text{C}$  and sintering then took place at approx. 1,300  $^{\circ}\text{C}$  under an inert atmosphere. In the process solid bonds were produced in the spray granules and less solid bonds between the individual granule grains. Deagglomeration and classification into the desired grain fraction (for example 15 to 45  $\mu\text{m}$ ) finally took place. The powder thus obtained could be further processed by thermal injection in a known manner to form hard metal or components coated with an alloy-hard material composite.

20

### Example 10

Titanium powder with a mean particle diameter D50 of 100  $\mu\text{m}$  was processed according to the invention and analogously to Example 1 to form flakes.

25

The flakes were then further processed in a comminution step analogously to Example 1, 10 g  $\text{TiH}_2$  being added as the grinding agent to the Ti flakes used (original weighed in quantity: 150 g). After comminution grinding there was a fine titanium powder with a mean particle diameter D50 of approx. 15  $\mu\text{m}$ .

30

The titanium powder produced according to the invention could be further processed by conventional process steps to form mould parts. To protect against oxidation the

titanium powder produced according to the invention was stored in an organic solvent, for example n-hexane. Long chain hydrocarbons, such as paraffin or amines, were added prior to powder metallurgical further processing. For this purpose, the paraffin was dissolved for example in n-hexane, added to the powder  
5 and the n-hexane was then evaporated with continuous circulating of the powder. A superficial seal against uncontrolled absorption of oxygen was obtained thereby and the improvement in compressibility achieved. This procedure allows the titanium powder to be processed in air.

10 After processing in terms of powder technology to form mould parts by single-axle compression, removal of the organic constituents in a thermal treatment, thermal decomposition of the grinding aid and sintering to form substantially dense mould parts took place.

15 **Example 11**

Flakes made of an alloy 17-4 PH® (Fe17Cr12Ni4Cu2.5Mo0.3Nb) and which had been produced analogously to Example 1, were treated in a contrajet mill. The flakes had a particle diameter to particle thickness ratio of approx. 1,000:1 and a mean  
20 particle diameter D50 of 150 µm. The contrajet mill was operated with inert gas. Atomised spherical material, which had not been pre-treated, of the same alloy with a particle diameter between 100 and 63 µm was used as the grinding aid. The grinding chamber (volume: approx. 5 l) was filled with 2.5 l powder bulk volume (67 % by weight grinding aid and 33 % by weight flakes) and the grinding process  
25 initiated. The fine fraction produced was separated at 10 µm by corresponding adjustments of a sifter connected downstream of the mill.

In contrast to the earlier examples, comminution grinding and the generally required deagglomeration were performed in one step by the procedure described. A  
30 particular feature of this procedure is the use of characteristic or alloy-like powder that cannot, or may barely, be comminuted and which leads to an increased

application of energy in the grinding process and thus to an improved grinding effect.

### Example 12

5

An atomised Ni17Mo15Cr6Fe5W1Co alloy with a mean particle diameter of 100 to 63  $\mu\text{m}$ , which is commercially available under the name Hastelloy®, was mechanically treated in a high energy mill (eccentric vibration mill) under the following conditions:

10

- Grinding container volume: 5 l (diameter 20 cm, length approx. 15 cm)
- Ball filling: 80 vol.%
- Grinding container material: 100 Cr6
- 15 • Ball material: WC-Co hard metal
- Ball diameter: 10 mm
- Originally weighed in quantity of powder: 300 g
- Oscillation amplitude: 12 mm
- Grinding atmosphere: argon (99.998 %)
- 20 • Grinding duration: 2 h

Flakes were produced which had a diameter to thickness ratio of 1:2 and a flake thickness of approx. 20  $\mu\text{m}$ .

- 25 Comminution grinding then took place in a gas contrajet mill. During comminution particles which had a particle diameter of  $< 20 \mu\text{m}$  were removed by suitably adjusting a sifter connected downstream. A fine alloy powder which, after ultrasound treatment, had a mean particle diameter D50 of 12  $\mu\text{m}$  and a D90 value of 20  $\mu\text{m}$ , determined using a Microtrac® X 100, was thus produced.

**METHOD FOR THE PRODUCTION OF FINE METAL POWDER, ALLOY  
POWDER AND COMPOSITE POWDER**

**ABSTRACT OF THE INVENTION**

There is provided a method of producing a metal powder, alloy powder or composite powder having a mean particle diameter D50 of less than or equal to 25  $\mu\text{m}$ , as determined using a particle size measuring apparatus (e.g., a MICROTRAC X 100 particle size measuring apparatus) in accordance with ASTM C 1070-01. The method includes, first providing a starting powder having a mean particle diameter D50 of greater than 25  $\mu\text{m}$ . The starting powder is then subjected to a deformation step, thereby forming flake-like particles having a particle diameter to particle thickness ratio of between 10:1 and 10,000:1. The flake-like particles are then subjected to comminution grinding in the presence of a grinding aid.